equation.[34,35] Due to these reasons we regard ξ as an adjustable parameter. As shown by the chain line in Figure 7, the best-fit curve has been obtained by taking $\xi = 0.482$.

From the value of Δ for the branched PDCPO, the distribution of the chain lengths of branches, including the main chain, can be assessed in terms of eq 16. In this calculation, ξ and α are taken to be 0.482 and 0.62, respectively. The values of $M_w\,(\mathrm{b})/M_n\,(\mathrm{b})$ thus calculated are listed in Table I. As expected, $M_w\,(\mathrm{b})/M_n\,(\mathrm{b})$ is much larger than M_w/M_n for the whole molecule and increases with molecular weight.

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Registry No. Poly[oxy(2,6-dichloro-*p*-phenylene)], 26023-26-7; 2,6-dichlorophenol homopolymer, 25511-62-0.

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Notes

Concentration Dependence of the Translational Diffusion Coefficient of Unperturbed Flexible Chains

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The dynamic light scattering (DLS) technique provides direct and highly accurate measurements of the concentration dependence of the diffusion coefficient of a polymer in solution in comparison with other techniques such as sedimentation diffusion (ultracentrifuge, SD) or conventional diffusion over a wide range of polymer molecular weight M. With the results, the theories on the coefficient k_D for flexible chains in dilute solutions can be discussed in detail for the polymer models used and the treatment of the hydrodynamic interactions. In this note, we sum up the experimental results of k_D for linear, narrow-molecular-weight polystyrenes (PS) at the Θ temperature, including our recent data,[1] and point out a weaker molecular weight dependence of k_D^Θ than expected from the theoretical expressions ($k_D^\Theta \propto M^{1/2}$) of Pyun and Fixman,[2] Yamakawa[3] and Imai,[4] or the recent report of Mulderije.[5]

We may expand the diffusion coefficient D for monodisperse linear polymers as a function of concentration c (g cm^{-3})

$$D = D_0(1 + k_D^\Theta c + \ldots) \qquad (1)$$

where D_0 is the translational diffusion coefficient at infinite dilution and proportional to $M^{1/2}$. The theoretical predictions available at present for k_D^Θ may be expressed as

$$k_D^\Theta = -(k_f^\Theta + \bar{v}) \qquad (2)$$

with

$$k_f^\Theta = BN_A v_H/M = B'M^{1/2} \qquad (3)$$

where $\bar{v}$ is the partial specific volume of the polymer, k_f^Θ the coefficient of the concentration dependence of the friction coefficient, N_A the Avogadro number, and v_H the hydrodynamic volume of the polymer at infinite dilution. The Einstein–Stokes law expression for D_0

$$D_0 = k_B T/6\pi\eta_0 R_H \qquad (4)$$

and the relation at infinite dilution $v_H = (4\pi/3)R_H^3$ lead to the second equality in eq 3. Here, η_0 is the solvent viscosity and R_H the hydrodynamic radius of the polymer. Thus all the theories available require an $M^{1/2}$ dependence of k_D^Θ in the larger M region because $\bar{v} \simeq 1$ (cm^3 g^{-1}). The difference in these theories is revealed only in the magnitude of the constant value B in eq 3. The Yamakawa[3a]–Imai[4] (Y-I) theories for bead-spring model chains lead to $B = 1$, while the Pyun–Fixman (P-F) soft-equivalent-sphere model gives $B = 2.23$. Mulderije[5] has recently revised the P-F value as $B = 2.06$, moreover indicating $B = 1.60$, which is based on the study of the hard spherical particles.[6]

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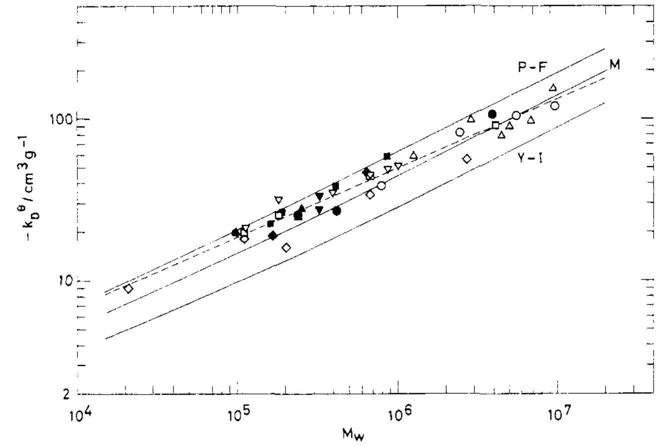

Figure 1. Coefficient k_D^{θ} for the concentration dependence of the translational diffusion coefficient plotted against M_w for linear narrow-molecular-weight polystyrene in Θ solvents. The open symbols represent the dynamic light scattering data: (○) Tsunashima et al.;[1] (□) Han;[7] (◇) King et al.;[8] (△) Jones and Caroline;[9] (▽) Frost and Caroline.[10] The filled symbols represent the sedimentation data: (●) Homma et al.;[11] (♦) Wales and Rehfeld;[12] (▲) Billick;[13] (▼) Kotaka and Donkai;[14] (■) Mulderije.[15] The broken line is the fitting curve of $-k_D^{\theta} = 0.13M_w^{0.43}$; curves $\mathrm{Y^{3a}}$–I,[4] P-F,[2] and M[5] are the theoretical ones represented by $-k_D^{\theta} = B'M_w^{1/2} + 1.1$ with $B' \times 10^2 = 2.73$, 6.09, and 4.37, respectively.

The experimental k_D^{θ} data, as we see now, differ from the above predictions. In Figure 1, we show the M_w (weight-average molecular weight) dependence of k_D^{θ} for narrow-molecular-weight PS under the Θ condition. The data with open symbols were obtained from the DLS technique[1,7-10] (eq 1) and the data with filled symbols were obtained from the SD technique[11-16] by using eq 2. Two facts become clear from this figure. First, no systematic difference in data due to the two experimental techniques is observed. This may indicate that both the intramolecular segment distribution of the individual separate molecules and the spatial distribution of the molecules in solution are not affected by the difference in the two diffusion processes. In other words, the short-time diffusion[17] seems negligible. Second, the k_D^{θ} data can never be represented by any single value of B as long as the $M^{1/2}$ dependence in eq 2 and 3 is adopted. The least-squares fitting of all of these 40 data points leads to a completely different M_w dependence of k_D^{θ} from theories and is expressed as

$$-k_D^{\theta} = 0.13M_w^{0.43\pm0.02}\ (\mathrm{cm^3\ g^{-1}}) \tag{5}$$

The broken line in Figure 1 represents this equation. The power of 0.43 is 14% smaller than the theoretical value of 0.50. Here, the solid curves Y-I, P-F, and M in Figure 1 represent the $\mathrm{Y^{3a}}$–$\mathrm{I^4}$ theory, the $\mathrm{P\text{-}F^2}$ theory, and the revised P-F theory (Mulderije[5]) with $B = 1.60$, respectively, in the form of eq 3. These B' values are $B' \times 10^2 = 2.73$, 6.09, and 4.37, respectively, which were estimated from our experimental result[1] for PS in *trans*-decalin at 20.4 °C (Θ temperature): $D_0M_w^{1/2} = (4.60 \pm 0.08) \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$.

As long as the equilibrium or averaged polymer conformation is independent of hydrodynamic interactions, the power law $k_D^{\theta} \propto M^{1/2}$ is predicted irrespective of the Gaussian (Y) or uniform (P-F) segment distributions of molecules. Recently, Akcasu's theory[17] based on the generalized Langevin equation has led to $B = 1.05$ for a prolate ellipsoid and $B = 1.26$ for a Gaussian chain, depending on the degree of correlations between intramolecular distributions of a pair of molecules. Olaj et al.[18] have reported the variation of the molecular radius with the separation distance of two molecules.

Recent hydrodynamic studies of hard spherical particles have strongly supported the value $B = 1.6$, theoretically[6,19] and experimentally.[20] In the range $M_w > 2 \times 10^6$, the k_D^{θ} data in Figure 1 seem to meet this requirement (line M). In the lower M_w region, deviation from this relation may occur. At the present stage, we cannot judge whether the data really reject the $M^{1/2}$ dependence over the entire M region as shown by the broken line in Figure 1 or show only a gradual change of the B value in eq 3 from one scheme to another, keeping the $M^{1/2}$ dependence as required from the theories. Recently, a difference of about 15% in D_0 between experimental[1,21,22] and theoretical[17,23,24] values at the Θ temperature has definitely become clear. A novel theoretical development on the hydrodynamic interactions in dilute polymer solutions should be required.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

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